Anisotropic Thermoelectric Response in Two-Dimensional Puckered Structures

Leonardo Medrano Sandonas, David Teich, Rafael Gutierrez, Tommy Lorenz, Alessandro Pecchia, Gotthard Seifert, and Gianaurelio Cuniberti

**INTRODUCTION**

Thermoelectric (TE) materials interconvert heat to electricity and are of great interest in environmentally relevant issues such as waste heat recovery and solid-state cooling. The efficiency of a thermoelectric material is measured by its figure of merit, $ZT = S^2GT/(\kappa_e + \kappa_h)$, where $G$ is the electrical conductance, $S$ is the Seebeck coefficient, $T$ is the absolute temperature, and $\kappa_e$ ($\kappa_h$) is the electronic (phononic) thermal conductance. The larger $ZT$ is the better is the performance of a TE material. Thus, promising TE materials should simultaneously have a high power factor (defined as the product $GS^2$) and low thermal conductance, ideally implementing an electron crystal and a phonon glass. Hence, in order for TE materials to become competitive with conventional refrigerators and generators, routes for tuning both transport quantities, electrical and thermal, need to be developed.

Nowadays, the ongoing quest for highly efficient TE materials has been centered on nanostructured materials. Thus, promising TE materials should simultaneously have a high power factor (defined as the product $GS^2$) and low thermal conductance, ideally implementing an electron crystal and a phonon glass. Hence, in order for TE materials to become competitive with conventional refrigerators and generators, routes for tuning both transport quantities, electrical and thermal, need to be developed.

Recently, phosphorene (or black phosphorene), one of the newest member from the family of 2D materials, has been successfully produced by mechanical exfoliation from bulk black phosphorus. The main feature of phosphorene is its puckered honeycomb structure, which leads to electronically relevant properties such as a nonzero bandgap of $\sim 1.1$ eV, large current on-off ratios, high charge mobility, and fast photoresponse. Moreover, anisotropic behavior of its physical properties has been demonstrated. In this respect, Luo et al. have reported anisotropic in-plane thermal conductivity of suspended few-layer black phosphorus measured by micro-Raman spectroscopy. Here, it was also found that, independent of the number of layers, the thermal conductivity for the zigzag (ZZ) direction is larger than for the armchair (AC) direction; for black phosphorus films thicker than 15 nm values of $\sim 40$ and $\sim 20$ W/mK for ZZ and AC directions, respectively, were reported. This effect has been theoretically verified by using the Boltzmann transport equation (BTE) and nonequilibrium Green’s function (NEGF) techniques. Electronic anisotropy has also been experimentally observed in layered black phosphorus. The results indicate that the AC direction is the most preferable electron transport direction. Taking advantage of these anisotropic properties, Fei et al. have shown, by performing first-principles band structure calcu-

Supporting Information
lations, that the thermoelectric performance of phosphorene can indeed be enhanced for transport in the AC direction, with values of $ZT \sim 1.0$ at room temperature.²⁹

In the past few years, a new family of 2D materials such as arsenene (a single layer of arsenic) and monolayer tin sulfide (SnS) has been discovered. They all may exist, like in phosphorene, orthorhombic puckered structures and semiconducting bandgaps, and, more interestingly, they all display anisotropic features in their physical properties. This has been reported e.g. in arsenene, where a different behavior for the electronic bandgap was found when uniaxial strain was applied along the ZZ and AC directions.³¹ A recent theoretical study by Zeraati et al. in orthorhombic arsenene has also shown, by solving the BTE, a highly anisotropic thermal conductivity at room temperature where the ZZ direction is the preferred direction for thermal transport ($\sim 30.4 \text{ W/mK}$).³⁴

Unlike arsenene, SnS nanosheets have been successfully synthesized by several techniques.³⁵,³⁶,³⁷,³⁹,⁴⁰ It has also been found that SnS thin films display a strong angle-dependent Raman response, indicative of anisotropy in their optical properties.³⁹,⁴⁰ The large Seebeck coefficient and the low thermal conductivity theoretically found in SnS bulk produce comparative thermoelectric performance compared to SnSe bulk,³⁷,³⁸,³⁹,⁴¹ which has been claimed to be an excellent candidate for thermoelectric devices.³⁸ It has also been reported that the electronic bandgap of SnS increases as the number of layers decreases,³²,³³ but it is not clear how this tendency will affect the thermoelectric response. Moreover, Guo et al. have shown that the thermal conductivity for SnS bulk is very low compared to other 2D materials and is also anisotropic.⁴² Based on the studies performed in other phosphorene analogues,³⁷,³⁸,³⁹,⁴² it is expected that the anisotropic effect remains in its monolayer form. However, to the best of our knowledge, this statement has not been yet verified.

Motivated by the results reported above, we analyze here the influence of anisotropy on the electron and phonon transport properties of homo- and heteroatomic two-dimensional materials with puckered structures—phosphorene, arsenene, and SnS monolayers—with the goal of identifying strategies to achieve a good thermoelectric performance. To do this, we employ a density-functional based tight-binding (DFTB) approach combined with Green’s function techniques. Our results show that the thermoelectric response of the studied materials, quantified by the figure of merit $ZT$, is larger along the AC direction and that SnS monolayers display the highest $ZT$ values ($\sim 1.6$ at 300 K and $\sim 4.5$ at 800 K) followed by arsenene. In the next section, we describe the computational methodology and, then, proceed to discuss the results of the anisotropic thermoelectric properties of these materials.

## COMPUTATIONAL METHODS

Neglecting electron–phonon interactions, which would need a separate self-consistent nonequilibrium study, both electronic and phonon transport channels can be considered as independent from each other.⁶ Then, the electronic and phononic (ballistic) transport properties can be computed within the Landauer approach in terms of the corresponding electronic $\tau_{el}(E)$ and phononic $\tau_{ph}(\omega)$ transmission coefficients. Using nonequilibrium thermodynamics and series expansions of the electrical current in the low bias, linear response regime, closed expressions for the different electronic transport coefficients appearing in the definition of the figure of merit can be written as:

$$G = e^2L_0$$

$$S = \frac{1}{qT} \frac{1}{L_0}$$

$$\kappa_d = \frac{1}{T} \left[ L_2 - \frac{L_1^2}{L_0} \right]$$

where $q$ is the electric charge of carriers, which is positive for holes and negative for electrons. The functions $\tau_{el}$ are given in terms of the moments of the electronic transmission function:

$$L_m = \frac{2}{\hbar} \int (E - \mu)^m \frac{\partial^2}{\partial E} \sum_\epsilon \{ \mathcal{G}_\epsilon \} \ dE$$

with $f(E,\mu,T)$ being the Fermi–Dirac distribution function, $\mu$ the chemical potential, and $\hbar$ Planck’s constant.

For phonon transport, the corresponding linear thermal conductance is given by

$$\kappa_{ph} = \frac{\hbar^2}{2\pi k_B T^2} \int_0^{\infty} \omega^2 \frac{e^{\hbar\omega/k_BT} - 1}{(e^{\hbar\omega/k_BT} + 1)^2} \tau_{ph}(\omega) \ d\omega$$

with $k_B$ being the Boltzmann constant. The prefactor in front of the phonon transmission function is obtained by a linear expansion in the applied temperature difference $\Delta T$ of the quantity $N_B(T + \Delta T) - N_B(T)$, where $N_B$ is the Bose–Einstein distribution. Notice that while for electrons the relevant integration range is usually located around the Fermi energy of the system, computing the thermal conductance of the vibrational system requires an integration over the whole phonon spectrum. Both transmission coefficients $\tau_{el}(E)$ and $\tau_{ph}(\omega)$ can be calculated in a similar way by using Green’s function techniques.⁴⁶,⁴⁷ We use a common partitioning scheme for both electron and phonons by dividing the system into three regions, namely left electrode, right electrode, and a central region. Notice however that the atomic composition of all three regions is the same for each given material; i.e., there are no effects related to interface scattering, neither for electronic nor for phononic degrees of freedom. The electron transmission coefficient $\tau_{el}(E)$ is then calculated as

$$\tau_{el}(E) = \text{Tr}(G \Gamma_L G \Gamma_R)$$

where the retarded Green’s function $G'$ is obtained from the Hamiltonian $H$, $G' = (E I - H - \sum_{\epsilon} - \sum_{\epsilon}^{-1})$, and the broadening functions $\Gamma_{L/R} = i[\sum_{\epsilon} \sum_{\epsilon}^{-1}]$ with $\sum_{\epsilon}$ being the electrode self-energies. The phonon transmission coefficient $\tau_{ph}(\omega)$ is calculated in a similar way by the substitution $H \rightarrow K$ and $E \rightarrow \omega^2 I$, where $K$ is the dynamical matrix. Here, both the electronic Hamiltonian matrix and the interatomic force constants are obtained using the DFTB method as implemented in the DFTB+ software package.⁴⁸,⁴⁹ The DFTB method is based on density-functional based parameterization of a general tight-binding Hamiltonian. Hereby, the system eigenstates are expanded into a linear combination of atomic orbitals (LCAO) minimal valence basis set, which are determined from self-consistent atomic LDA calculations. Additionally, the effective Kohn–Sham potential is approximated as a superposition of localized potentials of neutral atoms; see the Supporting Information for additional details. A valence basis set has been used including the 3s, 3p, and 3d orbitals for phosphorus and the 4s, 4p, and 4d orbitals for arsenic. For SnS we used the 5s, 5p, and 4d orbitals for tin and...
the 3s, 3p, and 3d orbitals for sulfur. All crystal structures have been optimized by using the conjugate gradient method with a force-threshold criterion of $10^{-4}$ hartree per Bohr radius. Finally, the thickness of the monolayers are taken to be 5.24 Å for phosphorene, 5.5 Å for arsenene, and 5.6 Å for SnS.

To express the thermoelectric parameters using an experimentally accessible quantity, one can easily relate the chemical potential to the carrier concentration by using the following expression:

$$n = \int D(E) \frac{1}{e^{(E-E_F)/k_B T} + 1} \, dE$$

Here, $n$ is the carried density, $D_e$ is the electronic density of states obtained from the electronic structure calculations, $k_B$ is Boltzmann’s constant, and $T$ is the temperature. Additional details of the temperature dependence of the chemical potential for the 2D puckered systems are shown in the Supporting Information.

### RESULTS AND DISCUSSION

Black phosphorus, black arsenic, and SnS are layered materials with orthorhombic structure in which individual layers are stacked together through van der Waals interactions. Their monolayer form has four atoms per unit cell, as it is depicted in Figure 1. Each atom is pyramidally bonded to three neighboring atoms of the same (phosphorene and arsenene, for homoatomic) or different (tin sulfide (SnS), for heteroatomic) species forming a puckered-like honeycomb lattice. As shown in Table 1, the lattice constants computed with the DFTB approach quantitatively agree (error $\leq 5\%$) with those obtained at the full DFT level by other authors for all three materials.

#### Electronic and Phononic Band Structures

The electronic band structure of the puckered materials is displayed in the three central panels of Figure 1. For phosphorene, the valence-band maximum (VBM) occurs along the $\Gamma$–$Y$ path while the conduction-band minimum (CBM) is located directly at the $\Gamma$ point. This results in a bandgap of about 1.94 eV,
which is in agreement with other theoretical studies. In contrast to what is reported by Fei et al., we observe an indirect bandgap (i.e., a second valence-band edge at the \( \Gamma \) point) which is slightly lower than the VBM and CBM located at the \( \Gamma \) point. Despite showing a different type of bandgap to that observed in recent first-principle studies, our bandgap magnitude is nevertheless close to the reported values at a higher level of theory, e.g., using hybrid functionals for the exchange-correlation potential (see the Supporting Information for a more detailed discussion about the electronic band structure). Considering the underestimation of bandgaps in conventional DFT calculations, we believe that our results are within an adequate range to study the thermoelectric properties of these materials. We also remark at this place that the ballistic transport features of all the studied systems is less sensitive to the type of potential (see the Supporting Information for a more detailed discussion about the electronic band structure). Considering the underestimation of bandgaps in conventional DFT calculations, we believe that our results are within an adequate range to study the thermoelectric properties of these materials. We also remark at this place that the ballistic transport features of all the studied systems is less sensitive to the type of potential (see the Supporting Information for a more detailed discussion about the electronic band structure).

Table 1. Calculated Lattice Constants of 2D Puckered Materials along Zigzag (ZZ) and Armchair (AC) Directions

<table>
<thead>
<tr>
<th>systems</th>
<th>transport direction</th>
<th>other works (ZZ, AC) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>phosphorene</td>
<td>ZZ 3.49, AC 4.34</td>
<td>(3.28, 4.43), (3.32, 4.58)</td>
</tr>
<tr>
<td>arsenene</td>
<td>ZZ 3.81, AC 4.75</td>
<td>(3.68, 4.77), (3.69, 4.77)</td>
</tr>
<tr>
<td>SnS monolayer</td>
<td>ZZ 3.93, AC 4.51</td>
<td>(4.03, 4.26), (4.01, 4.35)</td>
</tr>
</tbody>
</table>

“For comparison, the lattice constants from other published theoretical studies are given. In general, the difference between the DFTB lattice parameters agrees quite well (error \( \leq 5\% \)) with those at the full DFT level.”

Based on the phonon dispersion analysis (see the right panels of Figure 1), all studied systems are mechanically stable and do not show imaginary modes. As one can see in the phonon spectrum, the acoustic branches display the typical dispersion of 2D materials: the longitudinal (LA) and transversal (TA) acoustic branches have linear dispersion as the wave vector approaches the \( \Gamma \) point, while out-of-plane ZA branches exhibit quadratic dispersion due to the rapid decay of transversal forces. Moreover, it also can be seen that the distribution and dispersion of the phonon branches for homoatomic puckered materials is almost identical, except for their maximum frequency value, which is a consequence of the mass difference between As (\( \sim 75 \) umu) and P (\( \sim 31 \) umu). In general, the DFTB phonon band structures for P and As agree quite well with those computed with DFT (the results are included in the Supporting Information). Only for SnS the high-frequency optical modes are shifted upward.

Comparing the slope of the acoustic branches (i.e., the group velocity) for ZZ (\( \Gamma \rightarrow X \)) and AC (\( \Gamma \rightarrow Y \)) transport directions, it is expected that these materials will display strong thermal anisotropy. For instance, the longitudinal acoustic (LA) branch in phosphorene shows a group velocity of 8.35 and 4.74 km/s along the \( \Gamma \rightarrow X \) (ZZ) and \( \Gamma \rightarrow Y \) (AC) directions, respectively, which are very close to previous DFT results. For arsenene, our values for ZZ-5.01 km/s and AC-2.71 km/s, are also in agreement with those reported by Zeraati et al.\(^{34}\) SnS monolayer gives group velocities of ZZ-6.48 km/s and AC-2.14 km/s. It is worth mentioning that, up to now, thermal anisotropy has only been reported for phosphorene\(^{24,29}\) and arsenene\(^{31,34}\) but not for SnS monolayers. On the basis of these results, we expect that SnS monolayers will display the largest anisotropy in the thermal conductance due to the predominance of acoustic modes in the thermal transport, and this may have an impact on its thermoelectric properties.

Transport Properties. All transport calculations have been carried out using periodic boundary conditions in the perpendicular direction to transport and with the same number of unit cells. Moreover, to avoid additional effects arising from different material compositions of the electronic and phonon reservoirs and of the scattering region, we have chosen the reservoirs to consist of the same material as the scattering region. With this, we can reveal intrinsic transport features of the different systems. The electron and phonon transmission spectra are calculated for each material along the zigzag (ZZ) and armchair (AC) direction at equilibrium conditions. As it can be seen in Figure 2a,b for both phosphorene and arsenene,

Figure 2. Transport properties. Electron and phonon transmission functions along the ZZ (blue line) and AC (red line with shadow) transport direction: (a, d) phosphorene, (b, e) arsenene, and (c, f) SnS monolayer, respectively.

the electron transmission functions for ZZ and AC directions are slightly different at regions near the band edges but become increasingly different around the band centers. Hence, we find a weak electron transport anisotropy, in agreement with previously reported DFT calculations for phosphorene.\(^{56}\) Interestingly, DFT as well as the DFTB calculations give distinctive different electron effective masses (DFTB: \( m^* = 0.47 m_e \)) along AC direction and 1.43\( m_e \), along ZZ direction, DFT: \( m^* = 0.17 m_e \) along AC direction and 1.12\( m_e \), along ZZ direction) which would suggest within a classical transport model a distinct anisotropy in the electron transport. The situation is different, however, for SnS, where the transmission of the conduction band is 2 times larger for the ZZ direction than for the AC direction, showing significant anisotropic electronic properties (see Figure 2c).

In the next step, we computed the phonon transmission function in the ballistic regime (see Figure 2d–f). As it is expected from the phonon dispersion analysis presented before, phosphorene and arsenene have relatively similar phonon
transmission functions (Figure 2d,e). The only differences are the phonon bandgaps (−67 and −45 cm\(^{-1}\), respectively) and the maximum frequency value in the phonon dispersion. Likewise, we have found that thermal transport in the ZZ direction is larger than in the AC direction for almost the whole frequency range, in agreement with previous studies.\(^{24,29,31,34}\) In particular, SnS monolayer turns out to display the strongest thermal anisotropy.

**Anisotropic Thermoelectric Response.** To gain additional insights, we plot in Figure 3a–c the Seebeck coefficient \(S\) as a function of the chemical potential \(\mu\) for the three systems at 300 K for both transport directions. We remark that \(\mu\) is positive for n-type doping and negative for p-type doping. \(S\) is symmetric with respect to \(\mu = 0\) for homoatomic structures, but in the case of SnS monolayer, it displays an asymmetric behavior for \(|\mu| > 2.0\) eV (\(\sim 1.36 \times 10^{-19}\) m\(^3\)), related to the breaking of electron–hole symmetry in the electronic structure. The SnS monolayer displays the maximum Seebeck coefficient at 300 K, \(\sim 1.45 \times 10^{-3}\) eV/K, followed by phosphorene (\(\sim 1.3 \times 10^{-3}\) eV/K) and arsenene (\(\sim 1.18 \times 10^{-3}\) eV/K). \(S\) \(\text{max}\) for SnS monolayer is comparable to that found for its bulk phase\(^{31}\) but larger than that computed for SnSe systems.\(^{38,41}\) For phosphorene, \(S\) \(\text{max}\) is smaller than the value reported by Fei et al. using BTE.\(^{29}\) Moreover, we have found that \(S(\mu)\) has a different behavior as a function of temperature for each material. For phosphorene and SnS monolayer, the \(\mu\) value at which the Seebeck coefficient becomes largest lies rather close to the charge neutrality point (CNP), its magnitude first increases and then decreases, and at 600 K, it has almost the same value to that obtained at room temperature. Whereas, for arsenene, the Seebeck coefficient reaches its maximum at even lower \(\mu\) values than in the two other systems, and \(S\) \(\text{max}\) is almost halved at 600 K.

It can be also seen that independently of the temperature, the Seebeck coefficient is nearly isotropic; i.e., it does not appreciably depend on the AC or ZZ directions (see Figure 3a–c). However, when combining the corresponding electronic conductances and Seebeck coefficients into the power factor (\(PF = S^2G\)), anisotropic features become more evident, as shown in Figure 3d–f. The anisotropy is clearer seen for positive \(\mu\) values, with larger PF in the ZZ direction. Notice also that the PF exhibits some sharp peaks at certain \(\mu\) values, corresponding to the positions of the subband edges. Unlike graphene, the maximum value of PF for puckered materials is not located on the vicinity of the edge of the first conduction band.\(^{58}\) Some higher peaks were also found at doping concentrations where the Seebeck coefficient is small; for phosphorene and arsenene such high values are obtained in the \(\mu > 0\) region, while for SnS they lie in the \(\mu < 0\) domain. Despite the nonuniform temperature dependence of the Seebeck coefficient with respect to \(\mu\), the PF increases with increasing temperature for the three systems. Thus, PF peaks widen and can overlap with nearest-neighbor peaks. It is also seen in Figure 3 that increasing the temperature decreases the anisotropy in the PF, which could be further exploited to tune the thermoelectric performance.

In fact, the high Seebeck coefficient combined with the remarkable anisotropic behavior displayed by the PF for arsenene and SnS monolayers, compared to those for phosphorene, could suggest better thermoelectric properties if only the electronic contributions are taken into account. These values are also higher than those theoretically obtained for novel two-dimensional materials such as monolayer transition-metal dichalcogenides\(^{15,17,59–61}\) and graphyne.\(^{14,58}\) However, to have a more accurate understanding of the thermoelectric response, we need to consider the influence of phononic contributions to the thermal conductance.

The contributions of electrons, \(k_{el}\) and phonons, \(k_{ph}\), to the thermal conductance are plotted in Figure 4. Here, to have a

![Figure 3](image1.png)

**Figure 3.** Thermoelectric properties. Chemical potential dependence of the Seebeck coefficient (\(S\)) and power factor (\(PF\)): (a, d) phosphorene, (b, e) arsenene, and (c, f) SnS monolayer, respectively. We plot the results for both zigzag and armchair direction at two different temperatures: 300 K (solid lines) and 600 K (dashed lines).

![Figure 4](image2.png)

**Figure 4.** Thermoelectric properties. Chemical potential dependence of the electronic (\(k_{el}\)) and phononic (\(k_{ph}\)) contribution to the thermal conductance: (a, d) phosphorene, (b, e) arsenene, and (c, f) SnS monolayer, respectively. We plot the results of \(k_{el}\) for both zigzag and armchair direction at two different temperatures: 300 K (solid lines) and 600 K (dashed lines). Here, we can easily see the thermal anisotropy in these 2D puckered materials, \(k_{ph-ZZ} > k_{ph-AC}\).
better comparison with other works, we have considered a length of 100 nm to convert thermal conductance [in units of W/K] into thermal conductivity [in units of W/mK]. For electrons (see Figure 4a–c), $\kappa_\text{el}$ strongly depends on $\mu$ and on the temperature. After increasing the temperature, we can see an increase in the electronic contribution, although the differences between ZZ and AC directions discussed in Figure 3 remain. Moreover, all three systems have similar values of $\kappa_\text{el}$. This behavior has also been found in other heteroatomic puckered materials (bulk).26 Regarding the phonon contribution $\kappa_\text{ph}$ (see Figure 4d–f), we have found that for very low temperatures ($T < 20$ K) the thermal conductance is independent of the transport direction, whereas when the temperature increases, $\kappa_\text{ph}$ increases (because of the excitation of higher modes) and anisotropic effects become more pronounced due to the increasing contribution of acoustic modes to thermal transport. For the three materials it turns out that the thermal anisotropy is stronger than the electronic one, the latter being almost negligible. The preferred direction for phonon thermal conductance is along the ZZ direction, which is in good agreement with previous works.23,29,34,42 As it is expected due to the strong anisotropy in its phonon transmission function, SnS monolayer displays the highest thermal anisotropy at 300 K, $P_{AZ} = \kappa_{\text{ph-ZZ}}/\kappa_{\text{ph-AC}} \sim 2.5$, followed by phosphorene ($P_{AZ} \sim 1.6$), which is slightly more thermal anisotropic than arsenene ($P_{AZ} \sim 1.35$). The $P_{AZ}$ value for phosphorene is slightly different from that obtained by employing DFT calculations,26,53 while for arsenene there is more discrepancy from that reported by Zeraati et al.,34 which is mainly due to the methodology used. In the latter work they employed self-consistent calculations to solve the Boltzmann transport equation.

Unlike the electronic contributions, $\kappa_\text{ph}$ remains constant above 200 K, independently of the transport direction, since the whole phonon spectrum has been already covered by the frequency integration in eq 5. Comparing both contributions, it can be seen that phonons are dominant in the thermal conductance only for $\mu$ ranges nearby the subband edges. It is worth mentioning that as previously discussed, we have found sharp peaks in the PF in those $\mu$ ranges (see Figure 3). Thus, the influence of anisotropy on the thermoelectric response will be governed by the thermal one. Since SnS monolayers display the most optimal ration of high power factor to small thermal conductance when compared with arsenene and phosphorene, we may expect that its thermoelectric performance may also be the best one.

Combining now all the transport quantities, we show the results for the figure of merit, $ZT$, at a fixed temperature of 300 K for ZZ and AC direction in Figures 5a and 5b, respectively. We can see that in all studied materials $ZT$ displays sharp peaks which are located at $\mu$ values inside the region where $\kappa_\text{el} < \kappa_\text{ph}$. For phosphorene and SnS, the closest peaks to the CNP ($\mu = 0.0$ eV) are located almost at the same $\mu$ values because of the similar bandgap energy ($\sim 1.95$ eV, see also Figure 1), whereas for arsenene, the main $ZT$ peaks appear around $|\mu| \sim 0.5$ eV ($\sim 8.0 \times 10^{16}$ m$^{-2}$). $ZT$ peaks for transport in the AC direction are higher than those corresponding to the ZZ direction. This is a consequence of the competition between the weak electrical and strong thermal anisotropy found in all three systems. Another important factor is their extremely low phonon thermal conductance compared to conventional two-dimensional materials, which helps to increase $ZT$. Thus, SnS monolayer, which has the lowest thermal conductivity and the highest power factor, displays the best thermoelectric performance in both transport directions, reaching $ZT = 0.95$ and $ZT = 1.6$ at 300 K for ZZ and AC directions, respectively. These values are larger than those found for another heteroatomic puckered material, SnSe monolayer,60 and its bulk phase.37,42 We have also found that arsenene has better thermoelectric performance than phosphorene, showing a maximum figure of merit $ZT_{\text{max}} \sim 0.85$ at 300 K. The $ZT$ for phosphorene is close to the reported by Fei et al. employing the BTE29 and higher than bulk black phosphorus.62 Unlike the homoeotomic materials, the main sharp peaks of the SnS monolayer are located at $\mu \sim -2.1$ and $-3.4$ eV ($1.445 \times 10^{19}$ and $1.452 \times 10^{19}$ m$^{-2}$, respectively; p-type doping), which are related to the subband edges of the electron dispersion (see insets in Figures 5a,b). In Figures 5c and 5d we then show the temperature dependence of $ZT_{\text{max}}$ in the ZZ and AC directions. SnS monolayer has the highest $ZT$ values for the whole temperature range, and at 800 K values as high as $ZT_{\text{ZZ}} = 2.9$ and $ZT_{\text{AC}} = 4.5$ are obtained. These values are comparable to those found for tailored graphene nanoribbons.63,64 It is worth noting that, despite having quite similar electronic transport properties, arsenene shows larger $ZT$ values than phosphorene due to its lower thermal conductance. Moreover, $ZT_{\text{max}}$ values are $\mu$ dependent, and they display a different behavior for each material after increasing the temperature. For instance, phosphorene shows a better thermoelectric performance for p-type doping, and $\mu$ corresponding to $ZT_{\text{max}}$ changes from $-0.98$ to $-0.93$ eV for transport in the ZZ direction and from $-0.98$ to $-0.90$ eV for the AC direction, whereas for arsenene, n-type doping turns out to be more efficient in maximizing $ZT$, and the chemical potential varies in the range of 0.72–0.50 and 0.55–0.43 eV for ZZ and AC directions, respectively. In the case of SnS monolayer, finally, p-type doping is more efficient to optimize $ZT$; the chemical potential changes from $-2.12$ to $-2.22$ eV for the ZZ direction and from $-3.42$ to $-3.28$ eV for the AC direction. These effects are closely related to the temperature dependence of the chemical potential at a given

![Thermoelectric properties](image)
carrier concentration (see Supporting Information for details). Hence, to get the large thermoelectric response displayed by the SnS monolayer, we need a strong p-type carrier concentration.

To further quantify the anisotropy of the thermoelectric response, we have defined the quantity $M_{AZ} = ZT_{AC}/ZT_{ZZ}$ and plot it in Figure 6. The $M_{AZ}(\mu, T)$ features are not symmetric with respect to the charge neutrality point, which indicates that the anisotropic features are dependent on the doping type. Thus, the maximum $M_{AZ}$ is found for phosphorene and arsenene at n-type doping, while for SnS monolayer at p-type doping. Despite having the weaker thermal anisotropy, arsenene displays the maximal anisotropic response, $M_{AZ} = 4.0$ at 200 K (Figure 6b), followed by SnS monolayer with $M_{AZ} = 3.5$ (Figure 6c). Moreover, we have found this anisotropic effect decreases when the temperature is raised. This happens mainly due to the temperature dependence of the electron transport properties and quantities related because the phonon thermal conductance remains almost constant for $T > 200$ K as shown in Figure 4. We have also observed that by increasing the temperature, besides improving the thermoelectric performance, the ZT peaks widen and, hence, reduce the gap around $\mu = 0.0$ eV. This effect has also been reported for other nanomaterials.6,29,44,58

### CONCLUSIONS

In conclusion, we have performed a detailed theoretical study of the thermoelectric response of phosphorene, arsenene, and SnS monolayers. As we have shown, these systems show no strong electronic anisotropy, but a strong thermal one, which consequently leads to a strong anisotropic thermoelectric response. SnS monolayers show the highest thermal anisotropy ($\kappa_{ph-AC} > \kappa_{ph-ZZ}$) as well as the largest figure of merit $ZT$ in both transport directions, attaining values of up to $ZT_{ZZ} = 2.9$ and $ZT_{AC} = 4.5$ at 800 K, which can be reached by tuning the chemical potential to have a strong p-type carrier system. $ZT_{max}(T)$ values for SnS monolayers are also larger than those reported for SnSe monolayers, which is accepted to be a material with a high potential for thermoelectric applications. We have also found that arsenene may be a good candidate for designing thermoelectric devices because of its high $ZT \sim 1.0$ along the AC direction at moderate temperatures. Puckered arsenene displays the strongest anisotropic thermoelectric response, despite the fact that it has the weakest thermal anisotropy. Hence, these new puckered materials can be considered to offer a new playground to fine-tune—e.g., through directional strain engineering or by producing nanoribbons—the thermoelectric response.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b04969.

Detailed description of DFTB method and comparison with DFT calculations (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail rafael.gutierrez@nano.tu-dresden.de; Ph +49 (0)351 4633 1419; Fax +49 (0)351 4633 1422 (R.G.).

**Notes**

The authors declare no competing financial interest.

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**Figure 6.** Quantitative analysis of the anisotropic thermoelectric performance of 2D puckered materials. We show the patterns of the temperature and chemical potential dependences of $M_{AZ} = ZT_{AC}/ZT_{ZZ}$ for (a) phosphorene, (b) arsenene, and (c) SnS monolayer. The region in black means that $ZT_{ZZ} < 0.01$. 

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